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THE PHOTOLYSIS AND FLUORESCENCE OF DIETHYL KETONE AND DIETHYL KETONE - BIACETYL MIXTURES AT 3130 Å AND 2537 Å

By David S. Weir

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THE PHOTOLYSIS AND FLUORESCENCE OF DIETHYL KETONE AND DIETHYL KETONE - BIACETYL MIXTURES AT 3130 Å AND 2537 Å[1]

By

David S. Weir[2]

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The photolysis of diethyl ketone and the photolysis and phosphorescence of diethyl ketone-biacetyl mixtures have been studied at 3130 Å and 2537 Å. The addition of biacetyl at 3130 Å decreases the photodecomposition of diethyl ketone and increases the phosphorescence of biacetyl. An energy transfer from excited ~~singlet~~ triplet diethyl ketone to biacetyl is proposed and there is evidence that the propionyl radical formed from the singlet state at 3130 Å is sufficiently "hot" to dissociate into an ethyl radical and carbon monoxide. At 2537 Å dissociation appears to occur from the initially formed upper singlet state and there is no evidence that the triplet state intervenes. A detailed mechanism is presented for the primary process in diethyl ketone and for the energy transfer between diethyl ketone and biacetyl.

Introduction

The vapor phase photodecomposition of diethyl ketone at 3130 Å has been extensively studied[3-12] and a comprehensive

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3. V. R. Ells and W. A. Noyes, Jr., J. Am. Chem. Soc., 61, 2492 (1939)
4. W. Davis, Jr., Chem. Revs., 40, 201 (1947)
5. W. Davis, Jr., J. Am. Chem. Soc., 70, 1868 (1948)
6. L. M. Dorfman and Z. D. Sheldon, J. Chem. Phys., 17, 511 (1949)
7. W. A. Noyes, Jr. and A. Finkelstein, Disc. Far. Soc., 10, 308 (1951)
8. M. H. J. Wijnen and E. W. R. Steacie, Can. J. Chem., 29, 1092 (1951)
9. K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, J. Am. Chem. Soc., 74, 714 (1952)
10. R. K. Brinton and E. W. R. Steacie, Can. J. Chem., 33, 1840 (1955)
11. J. E. Jolley, J. Am. Chem. Soc., 79, 1537 (1957)
12. P. Ausloos, Can. J. Chem., 36, 400 (1958)

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review of the primary process in simple ketones published.[13]

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13. W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, Chem. Revs., 56, 49 (1956)

The light emission from excited diethyl ketone has not been so well studied although Matheson and Zabor[14] have recorded an

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14. M. S. Matheson and J. W. Zabor, J. Chem. Phys., 7, 536 (1939)

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emission from 4360 Å to 5460 Å with a maximum around 5200 Å. Since the emission is similar to that observed with propionaldehyde, they have ascribed it to the diketone bipropionyl formed during radiation. This effect is similar to that observed in acetone where the green emission is due to biacetyl.

This paper presents the results obtained from an investigation of the primary process involved in the photodecomposition of diethyl ketone and of diethyl ketone-biacetyl mixtures and the energy interchange between excited diethyl ketone and biacetyl.

Experimental

Eastman Kodak diethyl ketone was used. The ketone was distilled under dry nitrogen through about thirty theoretical

plates and a middle fraction, constant boiling at 102.7°, retained and stored over anhydrous copper sulphate. The fraction was thoroughly degassed at dry-ice temperature in a vacuum line and the middle fraction retained from a bulb-to-bulb distillation. No impurities could be detected in the mass spectrum and vapor phase chromatogram. Eastman white-label biacetyl was dried over Drierite, degassed and fractionated in a bulb-to-bulb distillation. A vapor phase chromatogram gave impurities of less than 1%. Spectro Grade Eastman acetone was dried over Drierite, degassed and distilled in a grease-free vacuum system. No impurities could be detected.

For 3130Å radiation an Osram HBO Super Pressure mercury lamp operating at 76 volts direct current and 6·2 amps was used. A Hanovia S-100 Alpine Burner was used for wavelengths in the region of 2537Å. The light was collimated and stray radiation prevented from entering the cell by a series of screens. For 3130Å the filter arrangement described by Kasha[15] was used,

15. F. Kasha, J. Opt. Soc. Am., 38, 929 (1948)

supplemented by a pyrex plate and a Corning 9700 filter. A filter combination of chlorine, cobalt sulphate-nickel sulphate solution and a Corning 9863 filter was used to give radiation of approximately 2537Å. The quantum yields for diethyl ketone photolysis were corrected for biacetyl absorption and decomposition.

A T-shaped quartz reaction cell was used for photolysis and light emission measurements. The cell was 125 mm long with

a main window diameter of 38 mm and a fluorescence window diameter of 23 mm.

Transmitted intensities of the exciting radiation were measured on an R.C.A. 935 phototube connected to a Varian G.10 Graphic Recorder. Quantum yields were calculated against the CO yield from diethyl ketone at 105° for 3130 Å radiation and the CO yield from acetone at 120° for 2537 Å, both of which are unity under these conditions.[5,16] Light emissions were photographed on a Hilger quartz prism spectrograph using Eastman Kodak 103a-B plates for the biacetyl emission and 103a-O for the diethyl ketone emission. The intensity of the biacetyl emission seen through a Corning filter was measured on an R.C.A. 1P21 photomultiplier tube connected to an R.C.A. WV-84A direct current microammeter.

16. D. S. Herr and W. A. Noyes, Jr., J. Am. Chem. Soc., 62, 2052 (1940)

A conventional vacuum line was used. The products from the photolysis of diethyl ketone -- carbon monoxide, ethylene, ethane, and butane -- were collected and measured in a McLeod Gauge-Toepler pump arrangement.[17] The product photolysis were frozen in the cold finger of the reaction cell with liquid nitrogen for 15 minutes. The volatile products were then left in contact with a solid nitrogen trap for a further twenty minutes before the carbon monoxide was removed and measured.

17. A. N. Strachan and W. A. Noyes, Jr., J. Am. Chem. Soc., 76, 3258 (1954).

The nitrogen trap on the cell cold finger was replaced by a dry-ice-acetone trap and the two remaining fractions ethylene-ethane and butane were separated using a Ward still[18]. The C_2 fraction came off at about -155° and the C_4 fraction at about -115°. Four hours were required for the full separation of the butane fraction from the residual diethyl ketone and involved repeated warming of the ketone from dry-ice-acetone temperature to room temperature.

18. D. J. LeRoy, Can. J. Res., B 28, 492 (1950)

Results

The results were observed at two incident wavelengths, 3130Å and 2537Å. For the intensity measurements carried out at 3130Å, the filter combination described above was replaced by a pyrex plate to obtain a larger variation in incident intensity.

The absorbed intensity I_a is given in quanta/ml/sec as calculated from the cell volume and the rate of absorption.

3130Å: The rate of formation of the total fraction (C_2H_4 + C_2H_6) was measured. Individual values for C_2H_4 and for C_2H_6 were not obtained. At this wavelength it is to be expected that the rate of formation of C_2H_4 and of C_2H_6 will be the same at room temperature. If one-half of the total C_2 fraction is taken to represent the rate of formation of ethylene, then a value of 0.135 is obtained for the ratio of rate of C_2H_4 formation to rate of C_2H_6 formation. This value compares favorably with previous evaluations of this ratio[9,10,12].

The variation of biacetyl emission is given in microamps. This value is obtained from the difference in photomultiplier readings when the cell is empty and when the cell is full.

The primary quantum yields are obtained by considering the following reaction scheme:

$$C_2H_5COC_2H_5 = C_2H_5CO + C_2H_5 \quad 1.$$

$$C_2H_5CO = C_2H_5 + CO \quad 2.$$

$$C_2H_5 + C_2H_5 = C_4H_{10} \quad 3.$$

$$C_2H_5 + C_2H_5 = C_2H_4 + C_2H_6 \quad 4.$$

$$C_2H_5CO + C_2H_5CO = C_2H_5COCOC_2H_5 \quad 5.$$

$$C_2H_5 + C_2H_5CO = C_2H_5COC_2H_5 \quad 6.$$

$$C_2H_5 + C_2H_5COC_2H_5 = C_2H_6 + C_2H_4COC_2H_5 \quad 7.$$

$$C_2H_4COC_2H_5 = CO + C_2H_5 + C_2H_4 \quad 8.$$

Reactions 7 and 8 are not considered important under the contitions of the experiments. Reaction 8 is probably important only at low intensity and high temperature[19] and reaction 7

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19. A. N. Strachan, Ph. D. Thesis, 1954, Rochester, N. Y.

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which does not have a high activation energy[9] should be important only at low enough intensities. The reaction between C_2H_5 and $C_2H_4COC_2H_5$ radicals which would be expected to give mainly $C_4H_9COC_2H_5$ is also considered negligible.

The primary quantum yields are estimated from the sum of the quantum yields of the radical-radical reactions,

$$\Phi = \Phi_{C_4H_{10}} + 1/2\,\Phi_{C_2} + \Phi_{DK} + \Phi_{K} \quad 9.$$

where $\Phi_{C_4H_{10}}$, Φ_{C_2}, Φ_{DK}, Φ_{K} are the quantum yields of butane, ethylene + ethane, diketone formation, and ketone formation

respectively and ϕ is the calculated primary quantum yield.

From the overall reactions

$$C_2H_5COC_2H_5 = CO + C_4H_{10} \quad 10$$

$$C_2H_5CCC_2H_5 = CO + C_2H_4 + C_2H_6 \quad 11$$

$$2C_2H_5COC_2H_5 = C_2H_5CCCOC_2H_5 + C_4H_{10} \quad 12$$

$$2C_2H_5COC_2H_5 = C_2H_5COCOC_2H_5 + C_2H_4 + C_2H_6 \quad 13$$

$$\bar{\phi}_{DK} = \bar{\phi}_{C_4H_{10}} + 1/2\bar{\phi}_{C_2} - \bar{\phi}_{CO} \quad 14$$

From equations 3, 4, 5 and 6 the $\bar{\phi}_K$ can be calculated from equation 15:

$$\bar{\phi}_K^2 = \bar{\phi}_{DK}\left(\bar{\phi}_{C_4H_{10}} + \bar{\phi}_{C_2H_4}\right) \quad 15$$

Two assumptions are necessary for the derivation of equation 15. Firstly that the collision diameter of the ethyl radical is approximately one-half that of the propionyl radical and second that $S_b^2 = Sa.Sc$ where Sa, Sb and Sc are the steric factors involved in the reaction of two ethyl radicals, an ethyl and a propionyl radical and two propionyl radicals respectively. The first assumption cannot be greatly in error. The second assumption was tested using results obtained under conditions where the primary quantum yield is likely to be nearly unity, i.e. low intensity and high temperature. Since only $\bar{\phi}_{CO}$ and $\bar{\phi}_{C_2}$ were determined under these conditions $\bar{\phi}_{C_4}$ was estimated from the previously determined relationship $1/2\,\bar{\phi}_{C_2} = 0.135\,\bar{\phi}_{C_4H_{10}}$. From equations 9 and 14 and assuming $\phi = 1$, $\bar{\phi}_K$ can be estimated. From $\bar{\phi}_K$, $\bar{\phi}_{C_4H_{10}}$ and $1/2\,\bar{\phi}_{C_2}$ the ratio $S_b^2 / Sa.Sc$ can be calculated. The three values obtained for this ratio --0.76, 0.11 and 0.20 -- are within a factor of 10 of the assumed figure.

From 9, 14, and 15 the primary quantum yield can be estimated. The principal results at 3130 Å are as follows:

1. Emission from Diethyl Ketone and Diethyl Ketone - Biacetyl Mixtures -- A weak emission from about 3850 Å to about 4700 Å was observed from diethyl ketone. The emission was so weak that no structure could be observed. Oxygen appeared to decrease the intensity and to shorten slightly the emission from the long wavelength end. Temperature did not affect the emission but pressure increased the intensity without affecting the spectrum. With a mixture of diethyl ketone and biacetyl a very strong emission was recorded. This emission consisted of three bands with maxima at 5120 Å, 5600 Å, and 6000 Å. Because of the low intensity it was impossible to tell whether the addition of biacetyl produced any effect on the intensity or the spectrum of the emission.

2. Effect of Biacetyl on the Decomposition of Diethyl Ketone and on the Phosphorescence of Biacetyl -- These two effects are shown in Table I and Figure 1, respectively. Table I shows the effect of biacetyl pressure on the Φ_{CO}, Φ_{C_2} and Φ_{C_4} at 25° and on Φ_{CO} at 57°. The effect on Φ and Φ^1 at 25° are also shown where Φ is the primary quantum yield calculated by equation 9 and Φ^1 is the same quantity less the contribution from reaction 6.

Increase in the biacetyl presure has the following effects: (a) At 25° and 58° there is a decrease in Φ_{CO}, in $\Phi_{C_2H_4 + C_2H_6}$, and in $\Phi_{C_4H_{10}}$. At 25° limiting values of 0.45 for CO, 0.11 for ($C_2H_4 + C_2H_6$) and 0.40 for C_4H_{10} are reached at a

TABLE I

EFFECT OF BIACETYL ON THE PHOTOLYSIS OF DIETHYL KETONE

T = 25° and 58° Diethyl ketone pressure = 25 mm
Wavelength = 3130Å

Biacetyl pressure mm.	Ia quanta/ml/sec x 10^{12}	T°C.	Φ CO	Φ C_2	Φ C_4	$\frac{\Phi C_2}{\Phi C_4}$	Φ	Φ^1
0	1.56	25	0.71	0.18	0.65	0.28	0.919	0.77
0	1.56	25	0.72	0.18	0.65	0.28	0.882	0.76
0	1.56	25	0.73	0.19	0.66	0.29	0.917	0.78
0.3	1.56	25	0.57	0.14	0.54	0.26	0.806	0.65
0.5	1.56	25	0.52	0.14	0.50	0.28	0.788	0.62
0.6	1.56	25	0.53	0.14	0.50	0.28	0.761	0.61
1.25	1.56	25	0.45	0.11	0.38	0.29		
2.40	1.56	25	0.45	0.11	0.40	0.28	0.507	0.46
0.0	1.56	59	0.91					
0.58	1.56	59.5	0.82					
1.21	1.56	58.75	0.77					
2.42	1.56	58.0	0.73					
2.75	1.56	57.0	0.72					
3.0	1.56	57.0	0.73					

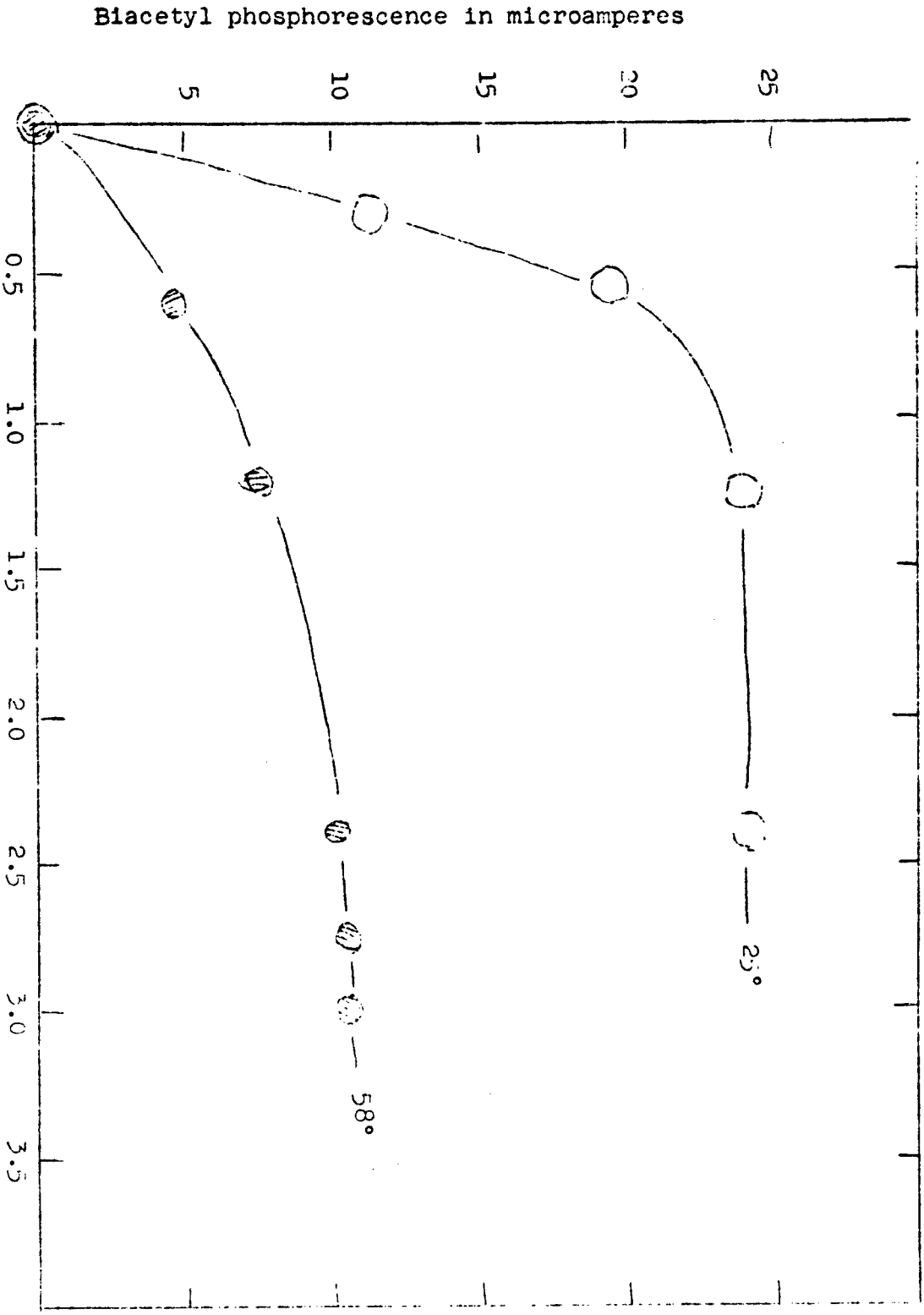

Fig. 1. Plot of biacetyl phosphorescence versus biacetyl pressure at 25° and 58° at 3130 Å

biacetyl pressure of 1.2 mm. At 58° a limiting value of 0.73 is obtained for Φ_I^{CO} at a biacetyl pressure of 2.0mm. No value for $\Phi_I^{C_2}$ and $\Phi_I^{C_4}$ were obtained at this temperature. The calculated values of Φ and Φ^1 also drop with increase of biacetyl pressure.

(b) At both temperatures the decrease in quantum yields is paralleled by an increase in biacetyl phosphorescence which reaches a limiting value at a biacetyl pressure of 1.2 mm at 25° and 2.0 mm at 58°. At 25° the limiting value is 24.2 microamps compared to 10.7 microamps at 58°.

(c) At 25° the ratio $\Phi_I^{C_2}/\Phi_I^{C_4H_{10}}$ remains constant. No figures were obtained for this ratio at 58°.

3. The Effect of Temperature on the CO Quantum Yield and Biacetyl Phosphorescence at High Biacetyl Pressure -- These effects are shown in Table II. An increase in temperature produces an increase in Φ_I^{CO} and a decrease in biacetyl phosphorescence in the region where Φ_I^{CO} and phosphorescence have reached a limiting value with respect to biacetyl pressure.

TABLE II

THE EFFECT OF TEMPERATURE ON THE CO QUANTUM YIELD AND BIACETYL PHOSPHORESCENCE AT HIGH BIACETYL PRESSURE

Diethyl ketone pressure = 25 mm Wavelength = 3130Å
Biacetyl pressure = 2.45 mm

Temp. °C	Φ_I^{CO}	Phosphorescence of biacetyl in microamps
27.5	0.45	24.2
33.25	0.51	20.75
41.5	0.58	16.2
57.0	0.72	10.1

4. Effect of Quanta Absorbed per ml. per second on the CO Quantum Yield -- Table III shows that at 25° and 60°

TABLE III

EFFECT OF QUANTA ABSORBED PER ML PER SECOND ON THE CO QUANTUM YIELD

T = 25° and 60°. Diethyl ketone pressure = 25 mm. Wavelength = 3130 Å.

Temp.°C.	$I_a \times 10^{11}$ quanta/ml/sec	Φ_{CO}	Φ_{C_2}
25	99	0.56	
25	25	0.71	
25	15.6	0.72	0.18
25	12.5	0.76	
25	1.79	0.83	0.21
60	99	0.87	0.21
60	25	0.94	0.22
60	15.6	0.93	
60	1.79	0.93	

a decrease in the rate of absorption per ml. increases the Φ_{CO}.

2537 Å. The results obtained at this wavelength are as follows:

1. Variation of Φ_{CO}, $\Phi_{C_2H_4 + C_2H_6}$, $\Phi_{C_4H_{10}}$ and Biacetyl Phosphorescence with Biacetyl Pressure in Diethyl Ketone -- Biacetyl Mixtures -- The above variations are recorded in Table IV. The following effects are observed:

TABLE IV

EFFECT OF BIACETYL PRESSURE ON THE CO, C_2H_4 + C_2H_6, C_4H_{10} QUANTUM YIELDS AND ON THE BIACETYL PHOSPHORESCENCE

T = 25°. Diethyl ketone pressure = 25 mm. Quanta absorbed = 2.97×10^{10} quanta/ml/sec. Wavelength = 2537 Å.

Pressure Biacetyl mm	Φ_{CO}	Φ_{C_2}	Φ_{C_4}	Φ_{C_2}/Φ_{C_4}	Phosphorescence in microamps.
0	0.91	0.30	0.86	0.35	0
0.58	0.89	0.29	0.81	0.36	0
1.2	0.91	0.28	0.81	0.35	0

1. Increase in the biacetyl pressure does not affect the Φ_{CO}, Φ_{C_2}, Φ_{C_4} nor the biacetyl phosphorescence which was not observed.

2. The ratio Φ_{C_2}/Φ_{C_4} remains constant but shows an increase over the values obtained at 3130 Å.

3. The Φ_{CO}, Φ_{C_2} and Φ_{C_4} increase with decreasing wavelength.

Discussion

Recent work[20] has led to the proposition of a detailed

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20. J. Heicklen and W. A. Noyes, Jr., J. Am. Chem. Soc., 81, 3858 (1959).

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mechanism of the primary process in acetone which fits the broad outline visualized by Noyes, Porter, and Jolley[13] to cover simple ketones. The proposed process involves: (1) absorption

producing an upper singlet state with a vibrational energy depending on the exciting wavelength. This upper singlet can either decompose, pass over to an upper triplet or suffer collisional loss of vibrational energy followed by fluorescence to the ground state or internal conversion to the triplet state.(2) molecules in the triplet state can either decompose with an activation energy, phosphoresce or undergo internal conversion to the ground state followed by phosphorescence. The addition of molecules such as oxygen or biacetyl would presumably remove this triplet state either in an energy transfer mechanism as suggested by Okabe and Noyes[21] or by direct reaction.[22]

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21. H. Okabe and W. A. Noyes, Jr., J. Am. Chem. Soc., 79, 801, (1957).

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22. G. B. Porter, J. Chem. Phys., 32, 1587 (1960).

Results obtained in the present work indicate that a similar mechanism may be involved in diethyl ketone. The proposed mechanism for diethyl ketone is given below:

$$K + h\nu = K_n^1 \qquad 16.$$

$$K_n^1 (+ M) = K_m^3 (+ M) \qquad 17.$$

$$K_n^1 + M = K_o^1 + M \qquad 18.$$

$$K_n^1 = \text{decomposition} \qquad 19.$$

$$K_m^3 + M = K_o^3 + M \qquad 20.$$

$$K_m^3 = K_o^3 \qquad 21.$$

$$K_o^1 = K_o^3 \qquad 22.$$

$$K_o^1 = K + h\nu_K^1 \qquad 23.$$

$$K_o^3 (+ K) = \text{decomposition} \qquad 24.$$

$$K_o^3 + K = 2K \qquad 25.$$

$$K_o^3 = K \qquad 26.$$

$$K_o^3 = K + h\nu_K^3 \qquad 27.$$

$$K_o^3 + B = B_o^3 + K \qquad 28.$$

$$B_o^3 = B + h\nu_B^3 \qquad 29.$$

where K is a normal diethyl ketone molecule, K_n^1 is a diethyl ketone molecule in the upper vibrational level of the excited singlet state, K_m^3 is a diethyl ketone molecule in the upper vibrational levels of the triplet state, K_o^1 is a diethyl ketone molecule in the low vibrational levels of the excited singlet state, K_o^3 is a diethyl ketone in the lower vibrational levels of the triplet state, B is a normal biacetyl molecule, B_o^3 is a biacetyl molecule in the low levels of the triplet state.

As in acetone[23,24,25,26,27] a weak blue emission is pro-

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23. G. M. Almy and S. Anderson, J. Chem. Phys., 8, 805 (1940).
24. R. E. Hunt and W. A. Noyes, Jr., J. Am. Chem. Soc., 70, 467 (1948).
25. G. W. Luckey, A. B. F. Duncan, and W. A. Noyes, Jr., J. Chem. Phys., 16, 407 (1948).
26. G. W. Luckey and W. A. Noyes, Jr., J. Chem. Phys., 19, 227 (1951).
27. H. J. Groh, Jr., G. W. Luckey, and W. A. Noyes, Jr., J. Chem. Phys., 21, 115 (1953).

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duced by light of wavelength 3130 Å. The diethyl ketone emission occurs in the same region as the acetone emission but

is much weaker. The addition of oxygen reduces the intensity slightly and appears to shorten the emission spectrum from the long wavelength end. This suggests the removal of some triplet state diethyl ketone but the effect is small and indefinite.

When excited by 3130 Å a mixture of diethyl ketone and biacetyl shows a very strong green emission with maxima at 5120, 5600, and 6000 Å. This is undoubtedly the biacetyl phosphorescence, thus indicating that the mechanism suggested by Okabe and Noyes[21] involving the energy transfer steps 28 and 29 is important. Corresponding energy transfer by the singlet state can be neither proved nor disproved.

As indicated in Table I and Figure 1, the addition of biacetyl at 3130 Å reduces Φ_{CO}, Φ_{C_2} and Φ_{C_4} and increases the biacetyl phosphorescence. Both effects reach a limiting value at the same biacetyl pressure. This would indicate the removal by the biacetyl of the triplet diethyl ketone thereby causing a reduction in the decomposition products and an increase in the triplet state biacetyl. An increase in the phosphorescence is therefore produced. If this is the case, it would appear that in the limiting condition where further addition of biacetyl causes no further effect, decomposition comes solely from the singlet state and the decrease in primary quantum yield is a measure of the removal of the triplet state. This conclusion is supported by the parallel increase in phosphorescence.

From the above mechanism it can be shown that

$$\frac{1}{\Phi_S} = 1 + \frac{(k_{17} + k_{18})(K)}{k_{18}} \qquad 30.$$

$$\frac{1}{\Phi_T} = X + Y\,(B) \qquad 31.$$

$$\frac{(B)}{Q} = X^1 + Y^1(B) \qquad 32.$$

where Φ_S and Φ_T are the yields for the singlet and triplet states respectively, (K) is the diethyl ketone concentration, (B) is the biacetyl concentration, Q is the phosphorescence efficiency (a purely arbitrary number obtained by dividing the phosphorescence in microamps by the quanta absorbed per ml per second) and X, X^1, Y, Y^1 are groups of constants. Equation 30 could not be verified due to experimental difficulty in obtaining the right kind of data. The data in Figures 2 and 3 show that relationships 31 and 32 respectively are reasonably well obeyed.

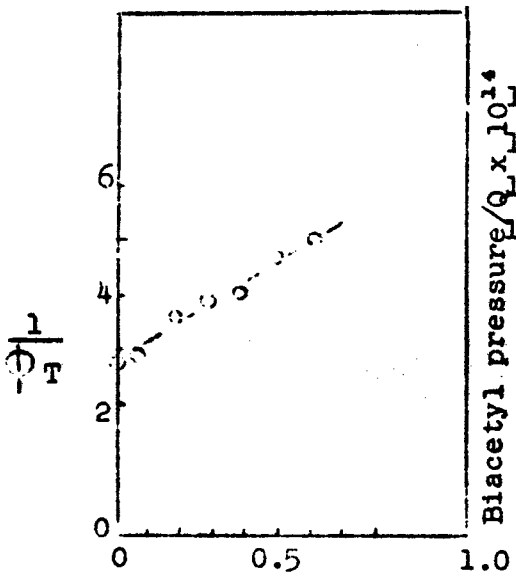

Fig. 2. Effect of Biacetyl on the triplet state yield

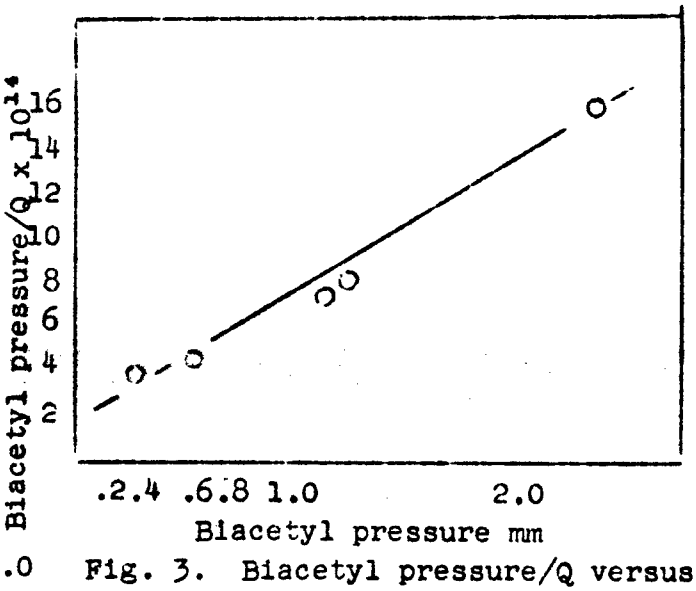

Fig. 3. Biacetyl pressure/Q versus biacetyl pressure

The propionyl radical formed from the singlet state at 3130 Å seems sufficiently "hot" to dissociate into an ethyl radical and carbon monoxide. Thus this part of the primary process leads to 2 C_2H_5 + CO. Evidence for this is found in the fact that the extrapolated value of $\frac{\Phi}{I}_{CO}$ at infinite intensity is virtually identical with the limiting value of $\frac{\Phi}{I}_{CO}$ when biacetyl is added. From the simplified reaction scheme 1, 2, 3, 4, and 6 and assuming (Et) = $I_a^{1/2}$ C, where C is a constant and (Et) is the ethyl radical concentration, it can be shown that $\frac{\Phi}{I}_{CO} = \alpha + C^1 I_a^{-1/2}$ where α is the fraction of

propionyl radicals which are "hot" and α^1 is a constant. At infinite intensity the intercept α tends to 0.44 at 25° and although only two points are available on the straight line portion at 60° a value near 0.78 is indicated at infinite intensity. While the singlet dissociate leads seemingly to 2 C_2H_5 + CO there seems to be some time lag in the formation of the second C_2H_5 and of the CO. In acetone[28] this is indicated

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28. J. N. Pitts and F. E. Blacet, J. Am. Chem. Soc., 74, 455 (1952)

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by the fact that addition of I_2 nearly completely suppresses CO formation even at 2537 Å.

If the addition of biacetyl suppresses dissociation from the triplet state equally effectively at all temperatures one is forced to the conclusion that the primary dissociation yield from the singlet state into ethyl and "hot" propionyl radicals increases with temperature and has an "apparent" activation energy of about 7.4 kcal. The meaning of this "apparent" activation energy is not clear but the following possibilities occur to mind: a) molecules with more vibration energy in the ground state absorb 3130 Å to dissociate much more rapidly than do molecules with less vibration energy. At first glance this might lead to the prediction of a very rapid change of singlet quantum yield with wavelength but this conclusion is subject to the reservation that the distribution of vibration energy

in the molecules produced in the upper singlet state might be very different depending on the mode of formation; b) the upper singlet state may last long enough before having its vibration energy equilibrated with the surroundings to suffer a dissociation with a true activation energy. We are here confronted with unknowns but from the meager knowledge we have concerning loss of vibration energy and the lifetime of the upper singlet state, such a unimolecular dissociation of the singlet state may not be excluded. In the case of acetone[27] the small change of fluorescence with temperature argues against this possibility; c) the triplet state biacetyl molecules may dissociate enough to yield carbon monoxide in adequate amounts at 60° to give the observed effect. Here again we are faced with an inadequate knowledge of the exact amount of energy transferred to the biacetyl. All of the evidence[29] from the behavior of pure

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29. G. F. Sheats and W. A. Noyes, Jr., J. Am. Chem. Soc., 77, 1421 (1955)

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biacetyl is against this explanation. Thus a) is the most probable but neither b) nor c) may be excluded. It might be pointed out in passing that the CO from the singlet state should rapidly become negligibly small as the temperature is lowered. Measurements of this effect would be difficult because of the low vapor pressure of diethyl ketone.

At 2537 Å addition of biacetyl produces no effect on

Φ_{CO}, Φ_{C_2}, or Φ_{C_4} and no biacetyl phosphorescence was observed. Dissociation must occur from the initially formed upper state and there is no evidence that the triplet state intervenes at all. The process again is essentially a split into an ethyl radical and a "hot" propionyl radical, the latter always dissociating to give carbon monoxide and a second ethyl radical probably after a finite time interval. Insufficient data were available to calculate Φ which however must be at least equal to Φ_{CO}. The high ratio of Φ_{C_2} to Φ_{C_4} is certainly due to the formation of C_2H_6 according to reaction 7. At the low intensities used, abstraction would be expected to be important. There is no evidence for or against "hot" ethyl radicals.

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